MECHANISM OF GASEOUS DETONATION

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1. Introduction

The phenomenon of detonation of gases has from the time of
its discovery in 1881 served as the subject of numerous investiga-
tions which have continued up to the present.

Interest in this phenomenon has been stimulated both by its
great technical importance, in particular for practices of explosion-
proofing in coal mines, pits, and in chemical industry, and by the
principal characteristics of this type of propagation of flame. As
is well known, the name detonation or detonation wave is given to
the phenomenon of propagation of a flame in detonating gaseous mix-
tures with a very great rate (1500-3500m/sec), where this rate re-
mains strictly constant for every given mixture and within broad
limits depends very little on the initial conditions (temperature,
initial density, form of the section of the pipe, and its dimensions)
The noticeable mechanical effects which accompany detonation indic-
ate that high pressures are developed in the wave, while high activ-

ity of the detonation flame gives evidence of the fact that the temperature in it considerably exceeds the temperature of a normal flame. Recently a tendency has been noted for a broadening of the circle of phenomena which are designated by the term "detonation," and for the inclusion in it of all combustion processes with a rate exceeding the velocity of sound (although not constant).

Detonation is usually caused by means of an explosion of a charge of an explosive substance, for example, lead azide, in a tube filled with a combustible mixture. In detonation under definite conditions a usual flame also develops in a closed tube, caused, for example, by an incandescent wire, an electric spark, etc.

Basic for the study of detonation was the photographic method in its various variants, which permitted not only the measurement of the rate of propagation of the detonation flame (according to the inclination of its trace on a moving film), but also the differentiation of details of its structure.

A sharp external distinction between detonation and the so-called "normal" flame corresponds to a profound internal difference in the mechanism of their propagation. The normal flame is propagated through thermal conductivity and diffusion of the active centers from the reaction zone ("the front of the flame") into fresh gas; hence its rate, determined by the appearance of molecular transfer, always is considerably less than the average thermal rate of the molecules, i.e., less than the velocity of sound, and the drop

in the pressure in the flame, caused by the change in the velocity of the substance in it, is always small.

An essential condition for detonation combustion appears to be the presence of a powerful shock wave with a powerful jump in the pressure and a supersonic velocity of the substance in it. The rate of propagation of detonation combustion is not related to diffusion and thermal conductivity and exceeds by several times the velocity of sound in the initial substance. The rate of propagation of a normal flame is known to be dependent on the rate of the reaction in it and the time of the reaction clearly enters into the equation for the rate, while the rate of detonation can be calculated with great accuracy from only the physical and thermochemical properties of the substance. Evidently therefore, the theory of gaseous detonation was originally developed by purely thermodynamic means. The whole specific chemical character of each given mixture, from which everything must be interpreted in a treatment of the limits of the phenomenon, was characterized by the concept of some absolute ignition temperature, lower than which the reaction takes place very slowly and higher than which it goes instantaneously. Only in connection with the development of the kinetics of gaseous reactions and chain theory, in which a leading role belongs to the Soviet school headed by N.N. Semenov, was the necessity perceived of taking into consideration the characteristics of all combustion processes due to the fact that the reaction takes place in time,

and the real possibility of such a consideration, based on the achievements of chemical kinetics, became apparent.

The current theory of detonation has as yet been limited chiefly to a consideration of the very fact of the development of the reaction in time in the detonation wave. Already this has permitted a better understanding of processes which take place in detonation combustion. A direct calculation of the characteristics of the detonation wave on the basis of kinetic data as yet remains very difficult (although the first attempts of such nature have already been made) both as a result of the insufficiency of kinetic data on the course of concrete reactions and because until now the very mechanism of the transfer (transmission) of the reaction in the wave has been unclear. This article is dedicated chiefly to just this mechanism of transfer of the reaction in gaseous detonation. Hence, we shall consider here only those stages of the development of theory and only those works which are essential to an understanding of the current state of this field and the task of further research in it.

2. Original Development of the Theory of Detonation

Berthelot,[1] who discovered the phenomenon of detonation, proposed that the chemical reaction (combustion) in the wave is transferred from layer to layer by particles of gas which possess a high velocity and an ability to produce the reaction. Measured rates of

detonation and the average velocities of thermal motion of mole-
cules which he calculated where the temperatures of the combustion
of the mixture seemed sufficiently close. Further precision of
thermochemical data, in particular heat capacities at high temper-
atures, showed, however, that the temperatures calculated by Ber-
thelot, and therefore the velocities of the molecules as well, are
considerably high.

Most of the succeeding researchers came to the conclusion that
the compression and initial heating of a combustible mixture by a
shock wave, accompanied by a wave reaction and maintained by it, ap-
peared chiefly in the transfer of detonation combustion. One of the
first to express such a viewpoint was our compatriot V. A. Mikhel'son
who, in his well known dissertation,[2] gave an interesting theoreti-
cal analysis of the phenomenon. Comparing detonation with the prop-
agation of shock waves, which had already been comparatively well
studied in his time, V.A. Mikhel'son came to the conclusion that a
detonation wave is a shock wave. However, in contrast to normal
shock waves in a gas, which are rapidly extinguished and degenerate
into sound waves, detonation is propagated in a sufficiently long
tube to any length, with a strictly constant rate. This is possible
because in detonation, as the shock wave is propagated, it liberates
the chemical energy contained in the combustible mixture and on ac-
count of this can maintain its constant rate. The liberation of
energy takes place in the following way. The shock wave, compressing

each succeeding layer of gas, takes it to such a high pressure and heats it to such a high temperature that an unusually fast, practically instantaneous reaction arises in the combustible mixture, and all the chemical energy of the combustible mixture at the shock wave front is transformed into thermal energy.

Imposing the condition of stationariness on such a shock wave, Mikhel'son obtained very interesting results, which remained insufficiently appreciated for many years. Hence, it remains for us here to consider the propagation of detonation in an infinitely long tube in the "inverse" system of coordinates related to the proton wave.

In such a system of coordinates, a tube with the fresh mixture (pressure P_0, density ρ_0, temperature T_0) will strike against a stationary wave with a velocity D of propagation of detonation relative to the tube. Let us construct two control sections, AA' and BB' (Fig. 1) before the shock wave front and at some distance behind it, in such a way that a drop in pressure, density, temperature, and velocity takes place between these sections. Let us recall that in the system of coordinates we have selected all phenomena are stationary, i.e., the state and velocity of the gas in every given section does not change with time. Let us also exclude from consideration any loss through friction or heat emission, considering them to be negligibly small. Then it is easy to draw up an equation for the conservation of matter and momentum. Designating the state

of the gas compressed by the wave (to the right of BB') by the subscript 1, we obtain (calculated for one square unit):

$$\rho_0 D = \rho_1 u = m, \tag{1}$$

where u is the velocity of the compressed gas relative to the wave front, and m is the mass velocity of the gas (the mass of the gas which passes in a unit of time through a unit in the surface of the wave). Let us write the equation for the conservation of momentum in the form

$$P_1 - P_0 = m \cdot D - mu = m^2 (v_0 - v_1), \tag{2}$$

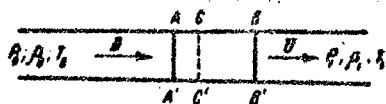where $v = \frac{1}{\rho}$ is the specific volume of the gas.

Fig. 1. Propagation of a shock wave in an inverse system of coordinates.

Consequently,

$$m = \sqrt{\frac{P_1 - P_0}{v_0 - v_1}}. \tag{3}$$

Due to the stationariness of the phenomenon, the same

relationship is correct for the gas in any intermediate section CC',
including also such sections where the chemical reaction takes place
(liberation of heat). Hence for any section

and

$$P + m^2 v = P_0 + m^2 v_0 = \text{const} = n^* \qquad (4)$$

$$m^2 = \frac{P - P_0}{v_0 - v}. \qquad (5)$$

It is evident that in the P-v diagram all points satisfying
equation (4) lie on the straight line AB, which passes through the
point P_0, v_0 at an angle whose tangent is $\tan \alpha = -m^2$ (Fig. 2).

Thus, all possible states through which the gas can pass in
the process of detonation (compression and combustion) lie on the
straight line AC. This circumstance, as will be shown later, is of
great importance for the current theory of detonation.

The most thermodynamically stable of all the states depicted
by the straight line AC is the state in which the entropy has a
maximum. Mikhel'son proposed that the gas in a detonation wave after
termination of the reaction passes into just this state. At the
point of the straight line at which the entropy is maximum (point D
Fig. 2), the straight line AC evidently relates to the isentropic
state. For the point of tangency, we can easily find from equation
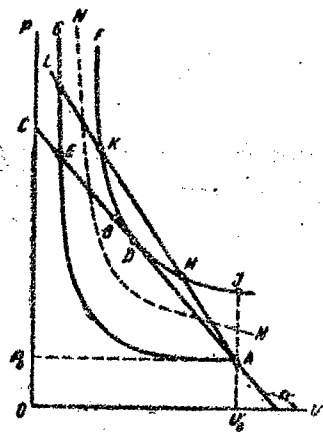
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Fig. 2. Adiabatic curves of Hugoniot for shock (curve GEA)
and detonation (curve FDJ) waves.

(4) and the equation of isentropy ($Pv^k = $ const.)

$$\frac{dP}{dv} = -k\,\frac{p}{v} = -m;$$

$$P_D = \frac{n}{k+1}$$

and for an ideal gas (Pb = RT),

$$T_D = \frac{k}{(k+1)^2}\,\frac{n^2}{R\cdot m^2}, \qquad (7)$$

Mikhel'son notes the curious circumstance that the maximum of the temperature lies above the point D. Indeed, the maximal temperature corresponds to the point of tangenoy of the straight line AC to the corresponding isotherm (Pv = const.; k=1), and the ratio of the pressure at the point of maximal temperature (Point B,Fig.2) to B_D will be equal to

$$\frac{P_B}{P_D} = \frac{k+1}{2},$$

i.e., P_B is always somewhat greater than P_D. For normal explosive mixtures in the combustion products $k \approx 1.2$, from which $P_B \approx 1.1\,P_D$. Correspondingly $T_{max} = T_B \approx 1.01\,T_D$.

Equation (7) can be simplified by neglecting the initial pressure P_0 in comparison with n. Indeed, $n = P_0 + m^2\,v_0 = P_0 + mD$; when $P_0 \ll mD$, which is the case for all the usual explosive mixtures, we can set $n \approx mD$, and then

$$T_D \approx \frac{k}{(k+1)^2} \cdot \frac{D^2}{R} \approx 0.27 \frac{D^2}{R} \approx 3.1 \cdot 10^{-5} D^2 \cdot M, \qquad (8)$$

where R and M are the gas constant and molecular weight of the combustion products, and D is expressed in m./sec. This formula is very convenient for an evaluation of T_D according to the known rate of detonation. If we consider that the velocity of sound $C^2 = kRT$ and if we utilize equation (8), then we come to the equation

$$D = C_D \cdot \frac{k+1}{k} \approx 1.8 C_D. \qquad (9)$$

where C_D is the velocity of sound in the detonation products. Let us find the relationship between the velocity of the wave relative to the compressed gas behind its front and the velocity of sound.

Utilizing equations (4) and (1), let us rewrite equation (6) in the form:

$$n = P_D + m u_D = (k+1) P_D.$$

Reducing and multiplying both parts by v_D, we obtain

$$m v_D \cdot u_D = u_D^2 = k P_D v_D = C_D^2.$$

from which

$$u_D = c_D. \qquad\qquad (10)$$

Thus, the rate of propagation of detonation relative to the reaction products behind its front is equal to the local velocity of sound. This property of the detonation wave, observed by E. Jouguet,[3] is of fundamental significance for its stability and distinguishes it from normal shock waves, the rate of propagation of which relative to the gas compressed in them is always less than the velocity of sound, as is well known. The wave of expansion of the detonation products, which is spread over some distance behind the wave front, moves with the velocity of sound c_D, and, due to the condition expressed by equation (10), can not reach the wave front and weaken it. Nor can any small (sound) disturbance overtake the front part of the wave.

The most detailed thermodynamic consideration of detonation was performed by Jouguet.

Considering the stationary detonation wave, we have already constructed for it an equation of conservation of matter (1) and of momentum (2). Let us now construct an equation for the conservation of energy. The stream of energy flowing in through section AA' (Fig.1) is equal to the stream of energy flowing out through section BB':

$$H_0 + \frac{D^2}{2} = H_1 + \frac{u^2}{2},\qquad (11)$$

where H is the enthalpy, which includes in the general case the chemical energy of the gas Q_{chem}.

$$H = C_p \cdot T + Q_{chem} = \int_0^T C_p \, dT + Q_{chem}.$$

For a mixture of a given chemical composition H is a function of Pv.

Excluding from the three equations (1), (2), and (11) with four unknowns (P_1, v_1, u, and D) u and D, and utilizing the equation of state Pv = RT, we obtain an equation of some curve lying in the surface P, v, where every point of this curve corresponds to some wave which satisfies the given initial conditions and all three equations (1), (2), and (11). In Fig. 2 such a curve AEG is presented for the case $Q_{chem} = 0$ (the adiabatic curve of Hugoniot for a pure shock wave) as is the curve JMKF for the case of a given $Q_{chem.} \neq 0$ (the adiabatic curve of Hugoniot for a detonation wave). The rate of detonation

$$D = m v_0 = v_0 \sqrt{\frac{P_1 - P_0}{v_0 - v_1}}$$

is given by the angle of inclination of a straight line constructed

from the point A ($P_0 v_0$) to a given point on the adiabat, for example K. As can be seen from Fig. 2, two points (two states) on the adiabat correspond to every rate. An exception appears to be the point of tangency, at which the secant AK turns into a tangent. This point is distinguished by the fact that in it the adiabat of Hugoniot also pertains to the isentropic state (the adiabat of Poisson) and is the point D already known to us. The point of triple tangency corresponds to the maximum of entropy on the straight line AC, but the minimum of entropy on the adiabat JF.

A comparison with experiments shows that in fact the state D, corresponding to the minimum possible rate of detonation, is always realized. Rarer adiabats, represented by points lying above the point D, are not realized. Indeed, in all waves corresponding to the points of the branch of the curve DKF, the velocity of the wave relative to the gas compressed in it is less than the velocity of sound ($u_K < c_K$). Therefore, if either the gaseous mixture is artificially placed in a condition corresponding, for example, to the point K, the rarification wave, which in the absence of artificial pressure from behind follows the compression* and is propagated with

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* The necessity of the subsequent rarification follows from the law of conservation of matter: At a given quantity of the substance in an unchanged volume an increase in the density in the

shock wave above the average value can take place only at the expense of a decrease in it behind the wave (at the front of the wave the gas is not excited). In order to avoid rarefication, it is necessary to create an artificial pressure, for example with the aid of a piston, which moves behind the wave. A simple exposition of the physics of shock waves can be found in 18. An experimental realization of detonation corresponding to the point K, in the presence of an artificial pressure, can be found in 38.

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the velocity of sound, will continuously overtake the front of the detonation and lower the pressure in it, so that it does not become equal to P_D. In the state D, as has been established, $u_D = C_D$; hence further weakening of the shock wave ceases and a stationary system is established.

For the points of the branch DMJ, there is the reverse relationship: $u_M > C_M$. Hence the rarer curves represented by this branch are not thermodynamically and mechanically prohibited, and the theory of Jouguet does not give any basis for their exclusion. The selection of the point D by Jouguet thus appeared to be theoretically arbitrary and was based only on experimental data.

For a long period of time a considerable portion of the experimental investigations of detonation were devoted to a verification of the theory of Jouguet. It was established that the rates

of detonation in the most diverse mixtures are found to be in good agreement with the calculated values.*   The pressures in the de-

* In an evaluation of the degree of agreement we must take into consideration that more or less reliable thermal data (dependence of the heat capacity or the temperature etc.) at very high temperatures have become attainable only over the last ten to twelve years.

tonation wave, measured by Campbell and co-workers[4] by the method of rupture of calibrated membranes, proved to be in good agreement with the calculated values. Thus, experiments have, as it were, confirmed the correctness of the theory of Jouguet.

For some time the question has been discussed of whether it is necessary to take into consideration the pressure of dissociation when determining the temperature and composition of the combustion products. The establishment of equilibrium, it would seem, requires time. Hence if, as is assumed in the theory of Jouguet, the combustion reaction (emission of heat) proceeds practically instantaneously, the succeeding endothermic reactions of dissociation should not influence the rate (rarification can not overtake the state D). Investigation of the rate of detonation at various

pressures, conducted by Dixon[5] and by A. C. Cokolik and K. I. Shchelkin[6] for different mixtures, and calculations of the rate of detonation taking into consideration dissociation, performed by Lewis and Friauff[7] and further, more extensively and accurately, by Ya. B. Zel'dovich and S. B. Ratner[8], have shown that equilibrium in a detonation explosion can be established and that therefore it is essential to take into consideration the dissociation of the combustion products in thermodynamic calculations.

As the circle of investigations has broadened the insufficiency of the thermodynamic theory of Jouguet, which has proved incapable of explaining a whole series of phenomena observed experimentally, has been more and more clearly revealed. In particular the weakness of this theory for an explanation of the ability of one mixture or another for detonation has been revealed. Not every combustible mixture is capable of detonation. It is impossible, for example, to force a mixture of carbon monoxide and air to detonate under normal conditions, although in the usual burner it burns very well. For any combustible mixture, for example for a mixture of hydrogen and oxygen, it is always possible at a given pressure to find such a relationship of the components at which this mixture, though remaining combustible, becomes incapable of supporting the propagation of a detonation wave. Such a limiting composition at $P_0 = $ latm. has obtained the name "concentration limit of detonation." Detona-

tion limits also exist for pressure (the propagation of detonation in a given mixture becomes impossible at a sufficiently low pressure) and for the diameter of the tube. Attempts to explain the existence of a limit by the fact that the temperature from the compression in the front of the wave to the limit becomes less than the temperature of ignition of a given mixture, as a result of which the mixture ceases to ignite (Jouguet, Crussard[9]), have proved to be quantitatively and qualitatively inadequate. The very idea of an ignition temperature, as of some absolute characteristic of a combustible mixture, is unreal and can not be considered out of the context of all the other conditions and, especially, without regard to the time of acceleration of the reaction (the time of inhibition, induction.), inherent in practically all real mixtures. The detonation theory of Jouguet operated by a concept of instantaneous (i.e., having a length of the order of the time of compression of matter in the front of the shock wave) ignition and instantaneous reaction of the mixture at the front of the detonation wave.

The development of chemical kinetics, of the theory of chain reactions, and of the theory of thermal explosion has made it possible to approach the investigation of gaseous detonation from new positions. In particular, a number of investigations of the limits of detonation of various combustible mixtures and of their detonation ability have been conducted (A. S. Sokolik, M. A. Rivin), leading to the conclusion that the reaction in the detonation wave must not be

considered as instantaneous. [10-11] The course of a reaction in time close to the limits becomes a factor determining the detonation ability of the mixture, which determines the very appearance of the limit. Such a point of view is fully confirmed by the observed influence of various factors on the limit of detonation. Thus, Laffit and Breton[12] showed that an increase in the initial pressure of a mixture of hydrogen and air from 1 to 8.7 atm. displaces the concentration limit respectively from 18.5% H_2 in the mixture to 14.5%. An increase in the initial temperature in this mixture (when $P_0 = 1$ atm.) to $300°$ displaces the limit lower than 17% H_2.[13] An increase in the initial temperature of a CO-air mixture to $\approx 500°$, according to the data of M. A. Rivin,[13] causes the detonation of this mixture, which does not detonate under normal conditions. An increase in the initial pressure or initial temperature leads respectively to an increase in the pressure or temperature of the gas compressed by the shock wave. Both these factors vitally influence the rate of the chemical reaction.

However, experiments in which the influence of small admixtures on the ability for detonation were studied seemed most indicative. After adding 1.3% H_2 to a non-detonating mixture of carbon monoxide and air, M. A. Rivin and A. S. Sokolik[10] obtained regular detonation in this mixture. The substitution of 1.3% CO for the H_2 practically does not change either the energetic or the physical properties of the mixture; however, as is well known, small admix-

tures of hydrogen have an unusually strong influence on the kinetics of the oxidation of CO. An analogous action on the detonation of the same mixture is exhibited by small (0.3%) admixtures of C_2H_2. A mixture of methane and air which does not detonate under normal conditions detonated in the experiments of M. A. Rivin[14] after the addition to it of 0.3% ethylene or 0.3% pentane.

Based on all these data, M. A. Rivin and A. S. Sokolik[10] proposed that the attainment of the limit is determined by the fact that the reaction in the wave is decelerated in proportion to the dilution of the mixture, while the extent of the reaction zone is increased. The detonation wave thus represents a shock wave in which gas is compressed, heated, and begins to react as a result of this. After some time τ has passed -- the induction period (time of inhibition), -- the presence of which is characteristic of the overwhelming majority of normal combustible mixtures, a rapid ignition and combustion of the mixture takes place. Thus, between the front of the shock wave and the zone of rapid reaction (ignition) there exists some gap which is equal to $d = \tau D$.* Assuming that the at-

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* In fact $d = \tau \cdot D \frac{\rho_0}{\rho}$, where ρ is the density of the gas compressed by the shock wave.

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tainment of the limit of detonation is determined by the fact that

the width of the gap d reaches a limiting size, and that upon further increase in it a steady propagation of detonation becomes impossible, the indicated authors gave a kinetic condition for the achievment of the limit in the form of the equation

$$\tau_{lim} = \frac{d_{lim}}{D}$$

Within the limits of the detonation $\tau \ll \tau_{lim}$, the width of the gap is much less than the limiting value, and hence propagation of detonation is possible.

3. Current Theory of Detonation

Attempts to develop quantitatively the qualitative ideas presented above within the framework of the old thermodynamic theory have shown that the introduction of new qualitative ideas of the course of the reaction in the wave demands a radical revision of the old theory and an analysis of the detailed mechanism of the process. Such a revision was made by Ya. B. Zel'dovich[15] in 1940 and led him to the following basic results.

The sharp change in pressure at a strong shock wave, as is well known, takes place at a width of the order of several lengths of the free path of a molecule of the gas, while the course of the chemical reaction, according to the current kinetic representations,

requires in every case more than a thousand collisions. Thus, for example, even under the conditions of the detonation wave (compression temperature 1700 - 1800° K.), only in one of ~ 200 collisions does the energy of the colliding particles prove to be sufficient for the reaction of atomic hydrogen with oxygen

$$H + O_2 = OH + O$$
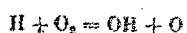
(a branched chain reaction), which, as is well known,[16] determines the rate of oxidation of hydrogen. To this must also be added the influence of the steric factor, thanks to which the probability of the reaction becomes significantly less. In the first moment after compression (directly after the front of the shock wave) the gas still is not capable of reaction. Hence, on the P-v diagram the state of the compressed gas directly behind the wave front is depicted by some point of the curve AEG of Fig. 2 (the adiabat of Hugoniot for a pure shock wave). At the same time, since every system is steadily propagated with the constant rate D, the point which depicts it should lie on the straight line AC. As can be seen from Fig. 2, both conditions correspond to only two points: the initial point A and the point E. In the course of time, as the reaction takes place and energy is given off, the depicting point strikes the intermediate adiabat, which corresponds to a partial liberation of heat, for example on the adiabat NN of Fig. 2, while at the same time remaining on the straight line AC. A complete liberation of heat, the state

of "detonation," corresponds to the point D. Thus, the gas in the detonation wave passes from the initial state to the state corresponding to point E, and then, as the reaction takes place, passes through a continuous series of states represented in the P - v diagram by the section of the straight line ED and, finally, strikes point D (the point of Jouguet), which corresponds to the final state of the detonation products. The distribution of the temperature, pressure, density, and concentration of the substance behind the front of the shock wave is shown schematically in Fig. 3, borrowed from a work of Ya. B. Zel'dovich.[17] The front of the shock wave, in which a sharp change in P, ρ, T, and u takes place, is denoted by E, while the state corresponding to the point of Jouguet (Fig.2) is denoted by D. Calculations show that $P_3 \approx 2\,P_D$, while P_D, in turn, is approximately twice as large as the pressure of an explosion of the same mixture in a closed volume.*

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*It is evident from Fig. 2 that n is equal to the section OC cut off by the straight line AC on the Y-axis.

An analysis, taking into consideration the presence of an unavoidable loss in heat emission and friction during the time the reaction takes place, was made by Ya. B. Zel'dovich with the conclusion that the state of detonation, which corresponds in all its

properties to the point D, is attained at the moment when the heat
content of the gas is maximal, i.e., when the evolution of heat
from the reaction is balanced by the loss in heat emission and
friction.* In this state precisely the fundamental property of

*Strictly speaking, the loss by friction is accompanied by
a change in the momentum of the mixture, so that in the presence
of friction equation (4) is also altered and the depicting point
does not lie on AC; this circumstance, which does not change in its
principal aspect, is considered in the work mentioned.[15]

detonation $u_D = c_D$, which ensures the mechanical stability of the
wave, is realized. It is very vital that in the reaction zone
(on the section AE of the straight line AC of Fig. 2) $u < C$, thanks
to which the maintenance of the shock wave front by the subsequent
combustion is possible. However, the adiabat on which D now lies
corresponds not to a total thermal effect of the reaction, but to
a liberation of an amount of heat equal to the difference between
that liberated at the moment D by the heat of the reaction and the
heat lost. Accordingly every adiabat constructed taking this loss
into account lies below the ideal adiabat FDT, and the inclination
relating to it is smaller; the rate of detonation in the presence of
a loss is likewise smaller than the ideal rate.

Steady detonation, corresponding to the upper branch of the curve DKF, is first of all impossible due to mechanical causes $(u_K < c_K)$. The lower branch of the curve DMT is also excluded in the theory of Zel'dovich in a completely obvious way: in order to arrive at the state M, the gas must first pass into L and then, after a series of successive states along the straight line AL, drop to M (Fig. 2).But in this process the substance should pass through the series of states of the portion KM of the straight line, in which the amount of heat should be greater than that contained in the reacting substance;* this obviously is impossible. A direct

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*Indeed, all the points of the section KM appear at the same time to be points of the adiabats lying above the adiabat FDT.

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abrupt transition from the state K to the state M is impossible, since a shock wave of rarefication is thermodynamically impossible (theory of Tsemplen[18]).

Thus, the introduction of the time of the chemical reaction into the consideration renders possible a strict basis for selection of the state D as the only one realizable in the steady detonation wave.

Recently articles have appeared in foreign literature, especially the American, in which the authorship of the current theory
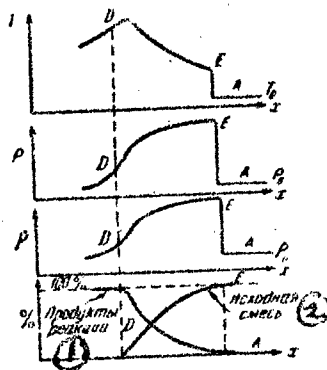
Fig. 3. Distribution of temperature, pressure, density, and
concentration in the detonation wave:
E - wave front; D - state corresponding to the point of
Jouguet
1 - Reaction products; 2 - starting mixture

of detonation, developed by Ya. B. Zel'dovich, is ascribed to John
von Neiman, who published his work in 1942 in a special edition
(OSRD Rep. No. 549, 1942). Let us recall that the exhaustive art-
icle of Ya. B. Zel'dovich with a full exposition of his theoretical
results[15] was published in 1940, and even before the war was
frequently cited in a number of Soviet works on detonation. Nonethe-
less, in the large survey article of Eyring and co-workers[19] devoted
to the problem of the stability of detonation of explosive sub-
stances, the authors, analyzing the material from the point of view
of the course of the reaction behind the wave front, nowhere men-
tioned the name of Ya. B. Zel'dovich, but often made special al-
lusions to Neiman. Kistiakoffsky and co-workers[20] do the same
thing in their recent work on detonation in a hydrogen-oxygen mix-
ture. Especially curious is the fact that these authors there refer
to the article of Ya. B. Zel'dovich of 1940* (which, therefore, was

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*Moreover, inaccurately, ascribing to him an assertion which
he did not make.

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known to them), but in connection with other problems (the trans-
fer of slow combustion in detonation).

Insofar as it is possible to judge from the literature avail-
able to us, von Neiman did not consider at all the most important

problem for this theory, detonation in the presence of a loss of energy from the reaction zone, while Ya. B. Zel'dovich resolved this question quite completely and rigorously. Now, in 1950, Kistiakoffsky[20] and co-workers as "the result of their experimental material," express (as their original hypothesis, "developing the concept of Neiman") the idea that in the presence of a loss, the point of Jouguet is obtained at the moment when the losses become equal to the intake of heat -- a result which was rigorously obtained by Ya. B. Zel'dovich in 1940.

The facts presented above are very indicative and clearly characterize the unceremonious attitude of some foreign researchers to the priority of Soviet scientists.

4. The Mechanism of Transfer of the Reaction

Is the accepted mechanism of the reaction (auto-ignition as a result of compression) the only one possible? Until now there have been no direct and convincing experimental data which would permit an unambiguous basis for the selection of the mechanism of ignition by pressure of a shock wave. Gasodynamic theory indicates only that combustion begins after compression by a shock wave; this, however, does not mean that it is caused by the compression. For example, such a scheme where behind the shock wave front, at some distance from it, the reaction is propagated in the form of a normal flame along the gas compressed by the wave is also logically possible.

In this scheme, the whole relationship of the theory of Zel'dovich and the whole scheme of the detonation wave are conserved, since they do not depend on the concrete mechanism of the course of the reaction and are obtained only from the single consideration of the course of the reaction in time and the selection of the state E as the first state realized within the detonation wave. However, the nature of the chemico -kinetic functions in the wave, the quantitative influence of the initial pressure, the initial temperature, and other factors on them will strongly differ in both cases, depending on whether the reaction is propagated by means of a flame or by means of auto-ignition as a result of compression.

A basic objection which is usually expressed against such a scheme boils down to the fact that a flame which is propagated by means of molecular thermal conductivity can not be propagated with the rate demanded by the conditions of the detonation wave. Indeed, the boundary of the reaction zone in the wave moves relative to the reaction products with the velocity of sound, while the normal rate of the flame is known to be much smaller than the velocity of sound. This objection, however, can be easily removed by assuming that the front of the flame is not flat. The normal velocity of the flame, of course, remains unchanged under this assumption, but the total amount of the burning substance increases proportionally to the surface of the flame, while the volume of the burning substance increases in the same proportion; hence, the path traversed by the

flame along the tube is equivalent. At the place where the flame front is distorted, as a result of the increase in the amount of substance burning in a unit section of the tube, an increase in the axial velocity of its motion arises, and, therefore, so does an increase in the pressure gradient, which in turn leads to the formation of individual jets and bursts of gas, which carry the flame out forward, etc. The rate of transference of the flame now is made up of the normal rate of its propagation along the motionless gas and the rate of the jets of gas which transfer the flame and can prove to be much larger than the normal rate. K. I. Shchelkin was the first to pay attention to the influence of the agitation of gas in the phenomena of detonation, first, in the origin of detonation.[37] K. I. Shchelkin also detected a strong influence of the roughness of the walls on the propagation of detonation.[32] For a more detailed exposition of the theory of the acceleration of the flame in the stream, see 21,22.

As L. D. Landau[23] showed, a flat flame front should become unstable under certain conditions, and auto-agitation should take place, leading to the development of the surface of the flame and an increase in the rate of propagation. Unfortunately, it is still quite unclear under just what conditions auto-agitation of the flame actually takes place. It is unclear whether a stable complex "shock wave - auto-agitated flame" is constructed. Hence, it is difficult to make an immediate definitive evaluation of the possi-

bility of the actual existence of such a mechanism of the propaga-
tion of the reaction in the detonation wave, although, as we shall
see further, there are many indirect indications that in a number
of cases it does take place.

Another possible mechanism for the transfer of the reaction
by turbulent flame was recently considered by M. A. Rivin.[24]

Let us consider schematically the nature of the motion of
the gas behind the detonation front. At the moment of compression
in the shock wave front AA, the gas (Fig. 4A) until then at rest,
is compressed and takes on a translational velocity W, which is the
same along the whole section of the tube. In proportion to the
motion along the tube (and, accordingly, the distance from the wave
front), the particles of gas adhering to the walls are retarded,
forming a boundary layer of increasing thickness. At some distance
from the place of the beginning of the flow, a disruption in the
laminar boundary layer takes place. The turbulent boundary layer
being formed gradually thickens until it encompasses the entire
section of the tube. Directly behind the place of the disruption
the stream consists of the very thin, so-called "laminar sub-layer"
which adheres to the wall and becomes the turbulent boundary layer
of increasing thickness, and (in the center) of the basic stream
with a constant value of the velocity. The velocity of the flow of
gas in the boundary layer varies from zero at the wall to the velo-
city W at the boundary of the boundary layer and the central nucleus

of the stream. The whole process close to the beginning of the flow introduces the picture of flowing around a thin plate, with the distinction that in the case under consideration, as a result of the constancy of consumption, the retarding of the gas close to the walls by the variation in pressure produces a corresponding increase in its rate in the nucleus, and thus a decrease in the rate of the wave relative to the gas in the nucleus $D - W_n$. The site of disruption in the boundary layer in physical hydrodynamics is determined by the condition that the number of Reynolds, consisting of the distance from the beginning of the detour in the flow to the place of the disruption, was equal to $5 \cdot 10^5$. For the case of typical normal detonation in the mixture $2H_2 + O_2$ (at an initial pressure of one atm.), this distance proved to be equal to approximately 0.3 cm. Accordingly, the distance from the wave front to the place of disruption of the boundary layer (the distance between the sections BB and AA) is equal to $0.3(D-W)/W \approx 0.06$ cm., while the time from the beginning of the compression $\mathcal{T} \approx 10^{-6}$ sec.

Let us suppose that auto-ignition of the mixture behind the wave front takes place somewhere to the right of BB, for example in CC. If it should turn out that the rate of propagation of the flame under the conditions of the turbulent layer (along its inner side), $w_{turb.}$, thanks to the redistribution of velocity in the stream and the large size of the pulsation,* is larger than the velocity of

*The pulsation rate is proportional to the difference in rates
of close-lying streams of gas. In the case under consideration,
the velocity of the gas varies over the extent of the thin boundary
layer from zero at the wall to $W = 0.8 - 0.85D$ at its inner bound-
ary. Pulsations of the order of hundreds of m/sec. correspond to
this. We should add that the normal velocity of the flame at a
high temperature of the gas in the shock wave should also be great.
For the influence of both these factors on the combustion rate see
21, 22.

the wave relative to the compressed gas, then the flame moving along
the inner side of the turbulent layer would approach the site of
the disruption (section BB) and the stationary state shown in Fig.
4, b would be attained. At some distance behind the wave front,
close to the place of disruption of the boundary layer, a circle of
flame is established which is propagated along the agitated layer
with the same velocity as the wave. From this circle the turbulent
flame is propagated along the whole section of the tube. In the
section CC the state of the products of the concluding combustion
corresponds to the point of Jouguet on the P-v diagram. The average
time from the beginning of the compression of the layer of gas
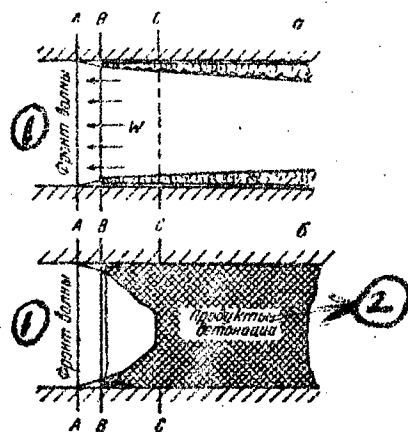(section AA') to the termination of the combustion in it will repre-

Fig. 4. A possible scheme for the transfer of combustion
by a turbulent flame behind the detonation wave front.

1 - wave front; 2 - detonation products.

sent in this scheme the effective time of reaction.

Thus, under the condition when $w_{turb} \gtrsim D - W$, it is sufficient if the time required for adiabatic ignition in the wave proves to be greater than approximately 10^{-6} sec., so that the compressed gas will begin to burn before ignition takes place. The emergence of a focus of combustion at some spot in the section (this also pertains completely to spin detonation) automatically makes auto-ignition difficult. A partial local consumption of the mixture in a given section corresponds to a decrease in the average values of the density and pressure for the section (the depicting point in the P - v diagram moves upward along the straight line of Mikhel'son) and leads to a corresponding isentropic drop in the temperature of the still unreacted portion of the mixture. The decrease in the pressure and the temperature should entail a hindrance of ignition, a displacement of it from the wave front, and, in the case of a sufficiently strong dependence of the rate of reaction on these factors, should also lead to a complete disruption of it.

It is easy to see that when satisfying both the three equations -- (1), (2) and (11), and the assumption that the reaction takes place in time from the initial state A to the detonation state D (Fig. 2), it is possible to pass not only through state E, but also directly from A along the section of the straight line AD. Although there are no general bases for rejecting such a scheme of the structure of the detonation wave, until now no satisfactory mechanism for

the transfer of the reaction has been proposed for it. In particular, all the attempts to construct a mechanism in which the reaction is transferred by active particles, which fly out of the detonation flame forward into the fresh gas, encounter one general difficulty: the distance of the action of such a bombardment cannot exceed several lengths of the free path, a distance at which all reactions should be able to take place; this, as we have seen above, is impossible.

We have dwelt on the consideration of this scheme chiefly in order to emphasize that the absence of general bases for the prohibition of the path AD leads to the necessity for a detailed analysis of every new mechanism of chemical reaction which might be proposed. There are no sufficiently weighty bases for asserting that the path AD is impossible in principle. This renders an experimental investigation of the structure of the detonation wave, which could conclusively resolve the problem of the mechanism of the uncoupling and transfer of the reaction and/of the path along which the state of the substance in the reaction zone varies, especially vital. Let us note that the mechanism of turbulent propagation proposed by the author[24] and considered above demands a rapid motion of the gas in front of the reaction zone. But only the shock wave, which spreads out with a supersonic velocity, is capable of setting the gas in motion; thus this mechanism is also depicted in the P-v diagram by the jump AE and the section ED, and not by the

direct transition AD.

The existence of limits of the propagation of detonation, according to the theory of transfer of combustion as a result of ignition by compression, is due to the fact that as the mixture is diluted (or the pressure or temperature is lowered, etc.), the reaction rate in the shock wave decreases, the reaction zone is extended, and the loss of energy in heat emission, friction, and incomplete combustion in the reaction zone increases. Beginning with some amount of loss, the stationary propagation of the complex "shock wave plus reaction" becomes impossible: the loss of energy leads to a noticeable drop in the rate, the point D slips downward, and the temperature and pressure in the wave drop. This leads to a sharp deceleration of the reaction, to an increase in the depth of its zone, and, consequently, to an even greater increase in the loss, etc.

Quantitative estimates show[15] that for real mixtures the limit should appear at comparatively small losses of energy -- of the order of ten per cent of the thermal effect of the reaction. Such losses can take place only when the reaction zone is extended to a depth of at least several diameters of the tube. Therefore, according to the theory, close to the limit and at the limit the zone of increased pressure and density, corresponding to the passage of the substance through a series of states on the straight line ED,

should have a significant depth and should yield comparatively simply to experimental investigation.[36] However, a comparison with the experimental material shows that long before the limit is reached the detonation wave takes on a radical difference from the "normal" structure, becomes "spin" detonation and that, in fact, we must differentiate two limits: the limit of "normal" detonation, when it passes into the "spin" detonation, and the limit of "spin" detonation or the absolute limit. Therefore, before dwelling in detail on the problem of the limits of detonation, we must turn to a consideration of the very phenomenon of "detonation spin."

5. Detonation Spin

"Detonation spin" was discovered in 1926 by Campbell and co-workers,[25] who noticed the wave properties of the line of the detonation wave front and the system of bands of intensified emission ("the band structure") on the photographs of detonation in a number of mixtures. The very simple and convincing experiments of Campbell and co-workers showed that the phenomenon of spin is not related to any external influences (oscillations of the walls of the tube, oscillations of the column of gas, etc.), but is inherent in the very phenomenon of propagation of detonation. In spin detonation the head of the flame photographed on film does not fill the whole section of the tube, but is propagated along it in a spiral path, where the flame itself has the form of a column rotating along

the periphery of the tube. Hence photographs of the flame, taken through a longitudinal split, also have a wave-like front. Sometimes, photographing an entire glass tube (without slit), it is possible to obtain on the film a clearly visible spiral, traced by the flame. On photographs on moving film, made through a circular slit in the end of the explosion tube, the flame leaves a trace in the form of a cycloid, which also indicates the propagation of the head of the spin in a spiral. Detailed measurements by Campbell, and then by Bone and co-workers,[26] and others have shown that the pitch of the spiral described by the head of the spin depends practically solely on the diameter d of the tube and is approximately equal to three diameters. Accordingly, the frequency of the spin (the number of rotations completed by the flame in a second), equal to $N = D/3d$, appears to be almost as characteristic for each given mixture as the rate of propagation of detonation D. It turned out that the spin can be many-headed, i.e., several focuses of the flame can be propagated simultaneously along several spiral paths of equal pitch. The heads are larger the larger the diameter of the tube and the further the mixture approaches the limit.

Based on high speed (scanning speed up to 1000m/sec.) photographs of spin detonation in a mixture $2CO + O_2$, Bone and co-workers assert that the horizontal system of spin bands is nothing but an optical illusion. In fact two systems of bands, differing from the head of the flame by their angle to each other, exist. Bright spots on the pho-

tograph at the places of intersection of these bands, blending together, give the impression of the horizontal bands visible on the usual photographs of spin detonation. One system of bands, directed along the movement of the wave, represents the trace of luminous gases (contaminated, evidentally, by dust), which move behind the front of the detonation. Another system of bands directed against the movement of the wave represents, according to Bone, the traces of the compression waves which arise in the detonation front as a result of periodic ignition of individual portions of the mixture, included in one coil of the spiral. The reaction of the detonation wave, according to these authors, is transferred from the flame front with the aid of radiation, absorbed by the compressed gas in the shock wave, which is propagated somewhat ahead of the flame. This Jacobi radiation produces local heating in the formation of active centers, as a result of which a local ("point") ignition occurs.

Without even speaking of the doubtfulness of the numerous hypotheses of the scheme of Bone, it does not explain the basic experimental fact -- the rotation of the head of the flame in the spiral along the walls of the tube. This fact is also persistently ignored in several other proposed explanations of spin, on which there is no need to dwell here.[39] The experiments of the authors cited on the propagation of detonation in tubes of rectangular and triangular sections are extremely important.[25,26] It has turned out that in such tubes the head of the spin is propagated approximately along

a described circle, while the afterglow preserves a band structure. The results of these experiments have permitted the authors to assert that spin is not related to a rotation of the entire mass of the gas as a whole, as was originally proposed by Campbell and co-workers.

The first rational idea of the mechanism of spin was expressed by K. I. Shchelkin[27] in 1945. Based on the instantaneous Teppler photograph of spin in the mixture $2CO+O_2$, conducted in the cited work of Bone and co-workers, on which it is visible that the shock wave front has a break, K. I. Shchelkin proposed that detonation spin is always related to the presence of a break in the shock-wave front and that the ignition of the mixture takes place just at the site of the break, where the pressure and temperature of the gas should be considerably higher than on the flat shock wave front. The break itself, as a result of interaction with the flame following behind, rotates along the shock wave front along the circumference of the tube. The spin, according to Shchelkin, arises when the limit is neared, when "ignition in the plane shock wave (as is the case in normal detonation) becomes impossible." From the site of ignition the reaction is propagated along the whole section, just as a normal flame.

On the basis of the detailed analysis of the phenomena which occur in the break, Ya. B. Zel'dovich[28] also came to the conclusion that the ignition of the gas takes place in the break of the shock

wave. The rate of propagation of the break relative to the gas flowing into it $D_1 > D$; hence the temperature and pressure in it are correspondingly higher, and the combustible mixture, which reacts with difficulty in the plane shock wave, should be easily ignited in the break. The break and the ignition in it should be considered as "super compressed" detonation, supported by the plane shock wave. Utilizing the circumstance that the head of the spin is propagated along the periphery of the tube, it is possible to show the essentially three dimensional phenomenon of spin in a first approximation in two dimensions.

In Fig. 5, borrowed from the work of Ya. B. Zel'dovich, the rectified peripheral shock wave front in this case is depicted. In a consideration of the figure, we should remember that the points S and S are in essence the coinciding points on the circumference (the place where the circumference is cut).

The break O_1O_2 is depicted as exaggeratedly large for convenience in the consideration. As can be seen from Fig. 5, motion of the break consists of motion along the axis of the tube with the velocity of the detonation D and movement along the circumference of the tube with the velocity $\sqrt{D_1^2 - D^2}$. As a result, the break moves in a spiral. A high temperature and pressure behind the front of the break produces a rapid reaction (ignition) of the gas somewhere on the line $O_1'O_2'$, and hence reaction products, the state of which should be described by some point of the detonation adiabat of
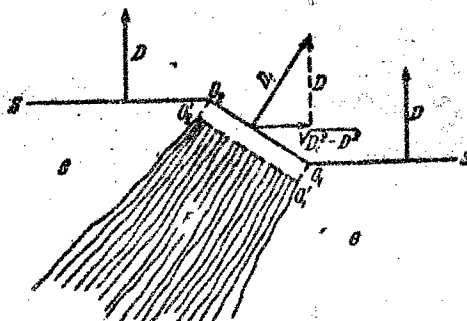
Fig. 5. Scheme of the spin wave. O_1O_2 is the break in the shock wave front.

Hugoniot (Fig. 6) already are found in zone F. Since the pressure of the combustion products P_F in F is equal to the pressure of the surrounding gas, compressed by the flat (more accurately, almost flat) shock wave P_B, the state of the reaction products corresponds to the

point F on the curve of Hugoniot. From the condition of stationariness of the propagation of the whole system, it follows that the ignition front $O_1'O_2'$ and the front of the transverse portion of the shockwave O_1O_2 should be propagated with the same velocity. Consequently, the state of the compressed gas behind the front of the transverse shock wave should correspond to the point O of our diagram.

A flame from zone F (Fig. 5) propagated along the compressed but unreacted gas, encompasses the entire section and transfers the gas to state D, i.e., to the state of normal detonation.

The scheme presented is only a first rough approximation, in which at the boundary of zone F a discontinuity in the velocity of the motion of fresh gas and the combustion products is obtained. For information on the equilibrium of the rates and pressures, we must impose a supplementary system of weak waves of compression and rarification, proceeding from O_1' and O_2'. As a result, a condition of stability of zone F arises: the velocity of the detonation products in zone F (in the "transverse wave") relative to the basic wave front should be equal or greater than the velocity of sound. For a calculation of the state of the gas in the "transverse" shock wave and a calculation of the angle of its inclination this velocity can be considered equal to the velocity of sound, to which the optimal condition of ignition (the greatest PT) in the wave front
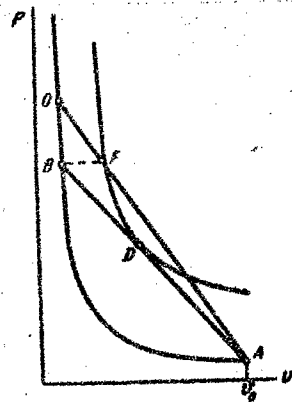
Fig. 6. Calculation of the state of the gas in the break of
the shock wave (in the head of the spin).

$O_1O_2O_1'O_2'$ corresponds. This assumption, however, has until now remained without theoretical basis, just as for a long time the selection of the point of Jouguet in the classical theory of normal detonation remained without basis.

The calculation of the angle α (Fig. 5), carried out for concrete mixtures has shown good agreement with experiments $\left(\alpha \approx 45°, \text{pitch of the spin} \approx 3d\right)$.

6. The Reaction Time and the Mechanisms of Its Transfer in the Detonation Wave.

In his very interesting investigation of the influence of the roughness of the wall on the course of combustion, K. I. Shchelkin[32] revealed that in a tube in which a wire is placed, wound in the form of a spiral and attached to the inner surface of the tube, the rate of detonation in a number of mixtures, such as $2H_2 + O_2$, $CH_4 + O_2$, etc., noticeably drops. A drop in the rate of 15 - 20% in comparison with the rate in a smooth tube is noted. The influence of roughness on the rate of detonation can be caused only by an increase in the loss in the wall (friction, thermal emission) from the reaction zone, up to the attainment by the gas of the state corresponding to the point of Jouguet. Hence from the experiments of K. I. Shchelkin which we have described it follows qualitatively that the reaction zone in the wave has a considerable extent, fully comparable in any case, with the dimensions of the roughness itself

(the diameter of the wire is approximately equal to 1.5 - 2.0 mm.). Such an extent of the reaction zone corresponds to a reaction time exceeding several microseconds. Utilizing the data on the drop in the rate of detonation in narrow tubes and comparing it with the losses in thermal emission and friction of the walls dependent on the diameter of the tube, we can draw the following conclusions on the reaction time:

1. The magnitude of the reaction in the mixture $2H_2 + O_2$ at an initial atmospheric pressure is proved to be of the order of five to ten microseconds. This quantity is fifty to a hundred times larger than the quantities calculated by A. I. Brodskiy and Ya. B. Zel'dovich[29] from data on the well-investigated kinetics of the oxidation of hydrogen in combustion.[16]

2. The dependence of the length of the reaction on a simultaneous variation in the pressure and temperature in the shock wave proves to be considerably weaker than it follows from the known kinetic data.[16,29] The reaction time depends little on the temperature and pressure.

3. The reaction time both for normal detonation and for spin detonation prove to be independent of the diameter of the tube.

The extremely low influence of pressure and temperature on the rate of the reaction observed is in poor agreement with the current representations of the kinetics of the corresponding reactions.

For an agreement with the classical theory of the transfer of the reaction by means of compression of ignition, some kind of supplementary assumption on the mechanism of the course of the reaction in the wave must be made, for example, the assumption of the presence of some kind of secondary exothermic reactions with a low temperature coefficient in the incompletely burned substance or the assumption of the presence of an abrupt redistribution of energy between the degrees of freedom in the reaction product, etc. The most probable is the assumption that in the mixtures investigated a mechanism which is radically different from the classical mechanism of transfer of the reaction by turbulent combustion takes place (see 24).

The critical values of the criterion of Reynolds observed in innumerable experimental works on this subject,[30,31] in which the flat flame front is auto-agitated ($Re_{cr.} = 5.10^4 - 10^5$), are of the same order as the value of Re behind the shock wave front at the limit of appearance of the spin. Thus, for the mixture 19% CH4 plus 81% O_2, the value of the criterion of Reynolds

$$Re = \frac{w_n d}{\nu}$$

where w_n -- the normal velocity of the plane probably does not exceed 10^5 (an accurate calculation is made difficult by the nec-

essity$_\wedge$ extrapolating, and thus the normal velocity under normal conditions of temperature and pressure in the shock wave is not too well known. However, as is now evident, in addition to the viscosity there are also certain factors which stabilize the flat front of the flame, and hence it can be expected that the stability is not dependent only on the quantity Re.

According to the scheme proposed by M. A. Rivin,[24] behind the wave front a zone of weak luminescence should follow, which represents the trace of the fine concentric turbulent flame (the "mantle" flame -- see Fig. 4, b), which then is either propagated along the whole section or produces by some method the appearance of an auto-turbulent flame (the front of strong luminescence*). The two types

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*The front of strong luminiscence here may not have noticeable irregularities: the magnitude of the irregularities (tongues) of the excited flame front can be very small in comparison with the diameter of the tube, since it should only appreciably exceed the thickness of the flame itself ($10^{-3} - 10^{-4}$mm.). Hence the surface of the flame can prove to be sufficiently well developed at low absolute dimensions of the tongue.

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of detonation, normal and spin -- correspond from this point of view

to two different mechanisms of transfer of the reaction -- by the turbulent flame and by auto-ignition as a result of compression in the head of the spin with subsequent complete combustion of the entire mixture. The conditions of the transition from normal detonation to spin detonation remain unclear and their explanation appears to be one of the basic tasks for further investigation. It is clear however that every change in conditions of the experiment which approaches the limit (the dilution of the mixture, a lowering in the initial pressure) makes the turbulent propagation and the appearance of autoturbulization difficult.

Is it realized under any conditions and in any systems with a non-spin plane auto-ignition behind the shock wave front? From the material presented above no logical bases for the elimination of such a mechanism follows. It is necessary only that the reaction time under the conditions of the shock wave be sufficiently small, i.e., that the depth of the reaction zone be less than the distance at which the disruption of the boundary layer takes place. In the experiments of K. I. Shchelkin cited above[32] it was noted that a roughness producing a drop in the rate of ten to twenty per cent in such mixtures as $CH_4 + 2O_2$ or $2H_2 + O_2$ has no influence on the rate of detonation in the mixture $C_2H_2 + 3O_2$. $\wedge$ When the mixture is extremely dilute (e.g. $C_2H_4 + O_2$) the influence of the roughness is quite clearly manifested. The absence of an influence of roughness on the rate indicates that the dimensions of the reaction zone are small, which should be characteristic pre-

cisely for the classical mechanism of transfer of the reaction. It will be very interesting to investigate detonation in the mixture $C_2H_4 + 3O_2$ both by the method of loss in narrow tubes and by other methods, and to verify the assumption of the classical mechanism of transfer of the reaction in this mixture.

Above we mentioned the kinetic calculation of the reaction time in the work of A. I. Brodskiy and Ya. B. Zel'dovich.[29] In this work a first attempt was made at a direct calculation of the reaction time in the detonation wave and the limit of detonation for a concrete chemical system -- the mixtures of hydrogen with air and hydrogen with oxygen.

These authors placed the now generally accepted scheme of chain oxidation of hydrogen between the first and second limits of ignition at the basis of their calculation:[16]

    I. $H_2 + O_2 = 2OH$ -- generation of the chains.

    II. $OH + H_2 = H_2O + H$ -- continuation of the chain.

    III. $H + O_2 = OH + O$ ⎫ -- branching of the chain.

    IV. $O + H_2 = OH + H$ ⎭

    V. $H + O_2 + M = HO_2 + M$ -- breaking of the chain in bulk.

All elementary processes related to the participation of the walls under the conditions of detonation are obviously eliminated. The rate of the elementary reaction of branching III, whose energy of activation is equal to 18,000 cal./mole, is of decisive signif-

icance for the rate of the reaction. The rate of the terminating reaction is independent of the temperature taken. Utilizing the known rate constants of the elementary reactions I - V, the authors calculated the rate of the reaction (rate of formation of the end product -- H_2O) and, respectively, the time of inhibition of the reaction * under the conditions of spin detonation in a hydrogen-air

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*As the characteristic time, a time is taken during the course of which one per cent of the substance succeeds in reacting. For a chain reaction this time practically does not differ from the time of the reaction of ten, twenty, or fifty per cent of the substance, since the basic part of the entire reaction time is taken up by its original acceleration (the time of inhibition, induction period).

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mixture at the lower limit (15% H_2). In Fig. 7 the calculated dependence of the inhibition time τ on the temperature is presented in the coordinates $\lg \tau$ -- T. As can be seen from the curve, above a certain temperature (approximately 1300° K. for the given concrete conditions) the reaction of breaking of the chain (reaction V) proves to be negligibly slow in comparison with the reactions of branching. However, beginning with a certain critical temperature and below, a sharp decrease in the rate of the reaction is observed

(the breaking of the chain through formation of HO_2 "extinguishes"
the branching and transfers the reaction onto another slower path)
and, correspondingly, a sharp increase in the reaction time (approx-
imately a thousand times in an interval of 100 degrees). This crit-
ical temperature is no different from the temperature of the upper
limit of the ignition at the pressure of the shock wave (as is well
known,[16] the appearance of an upper limit of ignition is related
precisely to bulk termination during triple collisions according to
reaction V). A. I. Brodskiy and Ya. B. Zel'dovich believe that the
decrease in the compression temperature at the head of the spin
proportional to the dilution of the mixture up to the critical temp-
erature determines the appearance of an absolute (independent of
the diameter of the tube) limit of detonation. The form of the de-
pendence of τ on T is also explained by the fact that close to the
limit the propagation of normal detonation is impossible, while spin
detonation can still be maintained. Indeed, the temperature of the
gas in the plane shock wave at the lower limit (15% H_2) proves to
be equal to 1000° K., to which a reaction time of the order of
milliseconds (Fig. 7) corresponds, i.e., very large for the condi-
tions of the detonation. At the head of the spin ($T_E = 1430^\circ K.$)
the reaction time is measured in microseconds and proves to be suf-
ficiently small to guarantee rapid ignition, which is essential for
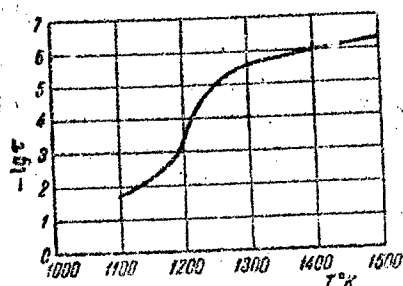steady propagation of detonation.

Fig. 7. The dependence of the reaction time τ in a mixture of H_2 plus air on the compression temperature at the head of the spin, according to Zel'dovich and Brodskiy.

The calculation of the reaction time in the plane shock wave in the detonation of a stoichiometric mixture $2H_2 + O_2$ performed by such a method lead the authors to a value $\tau \approx 7.10^{-8}$ sec. It has already been noted above that the calculated τ proved to be much less (50 to 100 times) than the measured combustion time in the wave.

If in the mixture $2H_2 + O_2$ the reaction in the normal detonation wave is transferred not by auto-ignition as a result of compression, but by turbulent combustion, as it was necessary to assume for an explanation of the experimental data, then it is not understood why a mixture which can ignite in the head of the spin at the limit of detonation cannot ignite in a flat shock wave in a stoichiometric mixture, although both the temperature and the pressure of compression in it are higher than in the first case. Moreover, this is not the only contradiction between the results of calculation and those of the experiments. The authors of the calculation themselves note the following two essential contradictions:

1. From the scheme of the reaction itself it follows that an increase in the pressure should narrow the limit, since the rate of the termination reaction V, proportional to the number of triple collisions, increases with pressure more rapidly than the rate of the branching reaction III, as a result of which the critical temperature is increased. Meanwhile, from the experiments of Breton[12] it is known that an increase in the pressure from 1 to 8.7 atm. lowers the limit from 18.5 to 14.5 per cent H_2 in the air. This fact is in apparent contradiction to the results of calculation.

2. For the same reason it is evident that with an increase in the initial pressure, for example in a stoichiometric mixture $2H_2 + O_2$, the limit of the propagation of the normal detonation would first be reached, and then that of spin detonation would be reached.

Meanwhile, experiments are known[33] in which this mixture detonated by the initial pressure of several hundred atmospheres. It is known also that the limit of propagation of detonation advances with a decrease in the initial pressure of the mixture. All these contradictions between the experimental data and the scheme of the reaction, as well as the results of the calculation, indicate that in a transition from high temperatures and pressures of the detonation wave, some factors become essential which are not taken into consideration in the general schemes of the reaction, developed on the basis of a study of the reaction in the region of promontory ignition.

An explanation of these factors and the causes of the divergence between experiment and calculation is of very great interest.

It is well known that in the transition of normal combustion detonation, detonation often arises somewhat in front of the flame front, as a result of the auto-ignition of the gas in the shock wave which has been formed. Sometimes this fact is considered as a confirmation of the fact that in a normal detonation wave the reaction takes place through ignition as a result of compression. However, the velocity of the wave close to the site of the auto-ignition is always greater than the velocity of the detonation wave established. A somewhat simplified scheme of the only published[26] detailed photograph of the site of the appearance of detonation in a mixture of $2CO + O_2$ is presented in Fig. 8. Detonation appears

at the point D, approximately 60 mm. in front of the normal combustion front, which moves with a velocity of 1275 m/sec. The rate of detonation, equal close to the site of appearance to 3260 m/sec., then decreases to 1980 m/sec. and only at a considerable distance from point D, after the establishment of spin, does it take on a stable value of 1760 m/sec. It is possible to assume that the high rate close to the site of the appearance is due either to the fact that the shock wave here is propagated along the gas, moving with a velocity of $3260 - 1760 = 1500$ m./sec. (i.e., along the peak of the adiabatic compression wave), or to the fact that at the moment of its formation the shock wave is strongly supercompressed in comparison with the stationary wave. And in both cases the calculation leads to values of the temperature and pressure at which auto-ignition takes place much larger than those attained in the stationary wave. From this the conclusion can be drawn that the pressure and temperature of compression behind the flat stationary wave front are insufficient for a rapid auto-ignition of the mixture. Consequently, the fact described above speaks more against the classical mechanism than in favor of it for a given mixture $2CO + O_2$.

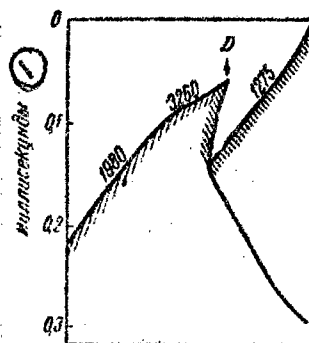Fig. 8. Scheme of a detailed photograph of the site of the appearance of detonation in the mixture $2CO \; O_2$.

7. Limits of Detonation

Let us return to the problem of the limits of propagation of detonation. Breton[12] and M. A. Rivin and A. S. Sokolik[34] noted that

when a limit is neared, normal detonation turns into spin detonation. Only spin detonation is observed in such difficultly detonating mixtures as mixtures of the majority of the hydrocarbons with air or of carbon monoxide with oxygen. Kh. A. Rakipova, Ya. K. Troshin, and K. I. Shchelkin[35] made a special investigation of the structure of the wave in a number of mixtures with limits and in all cases detected a spin. The authors indicated on this basis that the theory of the limit of detonation should be a theory of a spin limit.

A complete quantitative theory of the spin limit has not yet been created, since in essence a complete theory of the phenomenon of spin itself has not yet been constructed. Ya. B. Zel'dovich[28] and S. . Kogarko[36] relate the appearance of a limit to the spreading of the supercompressed gas from the break in the shock wave (the head of the spin) O_1O_1' O_2O_2' to the sides (see Fig. 5). Cooling of the gas in the break as a result of the spreading should be greater, the greater the ratio

$$\frac{\overline{O_1O_1'}}{\overline{O_1}_2} \sim \frac{\tau_c}{b},$$

where τ_c is the time of inhibition of ignition in the head of the

spin, and b is equal to the distance $\overline{O_1O_2}$. In order for rapid

ignition to remain possible, i.e. in order for the amplitude of

the wave in the break not to fall too low, it is necessary that as

τ_c increases (for example, as a result of dilution of the mixture)

the width of the break b correspondingly increases. At the same time

the quantity b should remain small in comparison with the diameter

of the tube; otherwise the surface SS of the basic shock wave takes

on too large an inclination to the axis of the tube (in the direction

of the displacement of the whole wave front), as a result of which

its normal velocity to the surface drops and the pressure behind its

front is lowered, which, in turn, leads to a drop in the pressure

and temperature of the super-compressed gas in the break, causes an

increase in τ_c , etc.

Thus, the spin limit should depend on the diameter of the

tube: the larger the diameter, the wider the break should be, the

more accessible the quantity τ_c, and the wider, consequently, should

the limit be. Here we should expect, independent of the diameter

of the tube, the spin will always be one-headed by the limit. Any

influence which decreases τ_c should act analogously to the increase

in the diameter. Consequently, for the spin limit the same qualita-

tive dependence should exist as that which is predicted by the theory

of normal detonation on the assumption of the "classical mechanism."[15]

Considering the subsequent propagation of the flame from the head of

the spin along the whole section, Ya. B. Zel'dovich and S. M Kog-

arko came to the conclusion that the total combustion time $\tau_{comb.}$ in the detonation wave, which was determined by the depth of the zone of increased pressure (the zone ED on Fig. 3), should be proportional to the diameter, as a result of which the specific loss in the wall (thermal emission, friction) should not depend on the diameter, and, consequently, should not influence the appearance of the limit (loss in the wall is approximately equal to $\frac{1}{d}$).

An investigation of the detonation limit of a hydrogen-air mixture in a tube of large diameter (300 mm.[36]) has shown that an increase in the diameter leads to a considerable broadening of the limits (up to approximately 15% H_2 when D equals 300 mm.). Measuring the pressure of the reflection of the wave from the end of the tube with the aid of crusher gages, the author showed that at the limit itself of the zone of increased pressure has a noticeable depth, of the order of $l = 15\,cm.$ The time that the gas remains in this zone, i.e. the combustion time $\tau_{comb.} = L/D - w = l\rho/D\rho_0 \approx 5l/D$. At a measured $D \approx 1500$ m./sec. we find $\tau_{comb.} = 5.10^{-4}$ sec. For a tube of such a large diameter this depth seems somewhat small, since it means that the normal flame from the head of the spin encompasses the whole section of the tube at a depth of approximately 0.5 of the diameter, for which the rate of propagation of the flame in a radial direction (for a one headed spin) should comprise $\frac{d}{\tau_{comb.}} = \frac{30\,cm}{5.10^{-4}\,sec.} = 600\,M./sec.$ In the case investigated, however, spin remains many headed. This

lowers the required radial velocity of the flame to 300 m./sec.,

which is still too much. In any case, these experiments represent

the first experimental, although still qualitative, evidence of the

existence of a zone of increased pressure, higher than that which

might be obtained at the point/Jouguet behind the detonation front.

The drop in temperature and pressure in the plane wave as

the result of a loss at the wall should lead to an almost propor-

tional drop in the temperature and pressure in the break of the

wave, and consequently, to a delay in the reaction in it and to the

appearance of a limit. It is curious that the quantitative criter-

ia of the appearance of a limit with such a mechanism of its ap-

pearance should remain the same as were deduced by Ya. B. Zel'dovich[15]

for normal detonation according to the "classical mechanism."

The theory of spin permits us to draw some conclusions on the

positions and possible dimensions of the break of the wave close to

the limit. In a rough approximation, represented by scheme in

Fig. 5, the rate of the influx of the gas in the front of the break

is equal to

$$D_1 = D_H^2 + D_T^2,$$

where D_H is the axial velocity of the propagation of detonation;

D_t is the peripheral velocity of motion of the break. The amplitude

of the shock wave is greater the greater the rate of its propagation. At the same time, at a given frequency of the rotation, the peripheral velocity is proportional to the distance of the break from the axis of the tube (the radius of rotation of spin), which we shall designate by x. The temperature and pressure of the gas compressed in the shock wave are approximately proportional to the square of its velocity. Thus

$$T \sim P \sim D_i^2 = D_H^2 + \left(\frac{x}{r}\right)^2 D_T^2 .$$

In Fig. 9 the line ACA represents the variation in the temperature in the break depending upon the distance of the head of the spin from the axis of the tube. It is clear that the most favorable conditions for ignition (the largest temperature) exists in the break when it is situated at the very periphery of the tube. At the limit of the detonation only such a position of it is possible.

By such a method it is also possible to obtain some idea of the possible radial dimensions of the head of the spin at the limit. It is easy to show that the same curve ACA of Fig. 9 represents the radial distribution of the maximum temperature attainable at the break. In fact, as has been indicated above, we must postulate still another condition for equality of the velocity of the detonation product at the head of the spin (relative to the wave front)
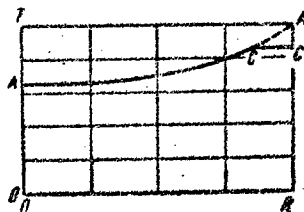
Fig. 9. Radial distribution of the maximally attainable
compression temperature of the gas in the spin break.

and the velocity of sound. Without devoting ourselves to detail,

let us note only that as a result of this the temperature in the

break T_c proves to be smaller than T_a, i.e., smaller than the

maximum temperature attainable at the optimum angle between the front

of the break and the plane wave. However, along the radius such a

temperature can exist only on the line CC. It is possible to assume

that the relationship of this length to the diameter of the tube is

an essential parameter in the theory of the spin limit.

Here the chemical-kinetic aspect of the theory of detonation

has chiefly been considered. The difficulty arising in the resolu-

tion of the problem of the nature of the motion of gas behind the detonation zone, of frictional retardation and thermal emission, is basically in the nature of calculations. Meanwhile, the problem of the mechanism of the transfer of the reaction in the wave, which until now has not been definitively explained, appears to be the principal physical problem. Hence the chief problem of investigation includes a definitive establishment of this mechanism and a quantitative confirmation of the theory. The possibility of direct study of the kinetics of chemical reactions at high temperatures and pressures with the aid of detonation, which has often been planned as a direct measurement of the rate of the reaction behind the front of a plane wave, in the light of the considerations presented seems doubtful. In all probability, information on the course of the chemical reaction under these conditions is limited to indirect data, obtained from measurements of the spin limits or from a comparison of calculated experimental rates.

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